VTT Technical Research Centre of Finland

Environmental, health and safety (EHS) aspects of cellulose nanomaterials (CNM)

Kangas, Heli

Published: 07/01/2018

Document Version
Other version

Link to publication

Please cite the original version:
Kangas, H. (2018). *Environmental, health and safety (EHS) aspects of cellulose nanomaterials (CNM)*. Biomaterials for Tomorrow, B4T 2018, Kochi, Kerala, India.

Environmental, health and safety (EHS) aspects of cellulose nanomaterials (CNM)

Heli Kangas

Biomaterials for Tomorrow B4T

Kochi, Kerala

January 7-9, 2018

VTT Technical Research Centre of Finland Ltd

75 years' experience in supporting our clients' growth with top-level research and science-based results.

Learn more:
www.vttresearch.com,
#vttpeople, @VTTFinland

- VTT is one of the leading R&D&I organisations in Northern Europe.
- We provide expert services for our domestic and international customers and partners, both in private and public sectors.

* Loikkanen, T. et al. Roles, effectiveness, and impact of VTT. Towards broad-based impact monitoring of a research and technology organisation. 2013. VTT, Espoo. VTT Technology 113. 106 p. + app. 5 p.

Net turnover and other operating income 269 M€ (VTT Group 2016)

Personnel 2,414 (VTT Group 2016)

Unique research and testing infrastructure

Wide national and international cooperation network

Motivation

Source: Uni-ball

- Due to their unique nano-specific properties, cellulose nanomaterials (CNM) have numerous potential applications.
  - replacement of fossil-based materials in packaging, deodorizing material in adult diapers, cell growing media…
- As bio-based materials, CNM are often assumed safe.
- However, their nano-specific properties may potentially make them hazardous towards humans and the environment.

Source: Stora Enso

Source: Deleon Cosmetics

Source: Natural Friends

Source: Nippon Paper

Motivation

- Biopersistence of long and thin high-aspect ratio fibers is known (case asbestos)
- Wood dust is a carcinogenic material
- Nanoscale features give rise to new material properties and biological behavior
  - Decreased particle size – improved penetration
  - Increased specific surface area – enhanced interactions with their biological surroundings

Examples of safety assessment at VTT

Case 1: Human health - Results on the toxicity of the smallest fraction of cellulose nanofibrils

Pitkänen, M., Kangas, H., Laitinen, O., Sneck, A., Lahtinen, P., Peresin, M.S. and Niinimäki, J. (2014) Characteristics and safety of nano-scale cellulose fibrils. Cellulose 21, 3871-3886. DOI 10.1007/s10570-014-0397-x

Background & approach

§ In our previous studies, CNF materials as such showed no indications of toxicity.

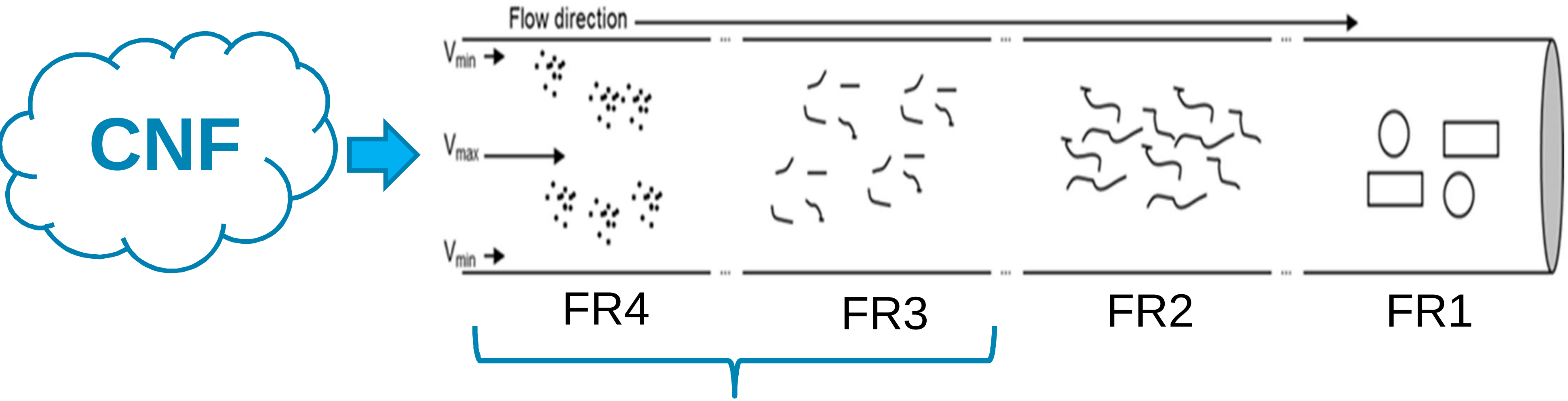
§ However, with fractionated cellulose nanofibrils, the smallest fraction showed indications of toxicity/slight toxicity.

- Due to cellulose nanofibrils?
- Due to the bacteria present in the sample?

ü Further testing was needed to confirm/disprove the slight toxicity effects observed

ü Finely fibrillated CNF was fractionated into separate size fractions ensuring that there was no bacterial contamination.

Fractionation of CNF



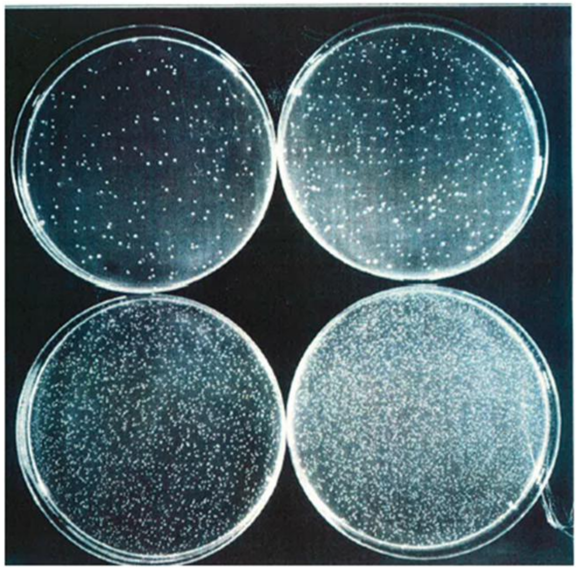
Original CNF

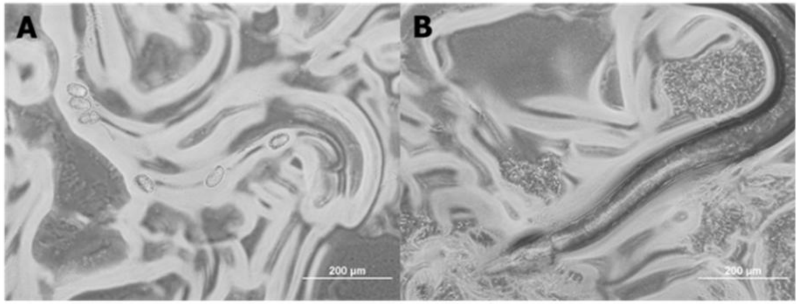
Combined sample for further tests

1. Finely ground CNF was fractionated using tube flow fractionation into four fractions
2. The finest material, FR3 and FR4, representing ~20 w-% of the original CNF, were collected
3. Fractions FR3+FR4 were combined and subjected to toxicity tests.

Toxicity testing of the nano-scale fibrils (FR3+FR4)

- Cytotoxicity *in vitro*
  - Highest tolerated dose (HTD)
  - Total protein content (TPC)
- Sublethality
  - RNA inhibition test
- Genotoxicity *in vitro*
  - Ames test
- *In vivo* testing with nematode model
- Biocide addition before testing (10 mg/l)

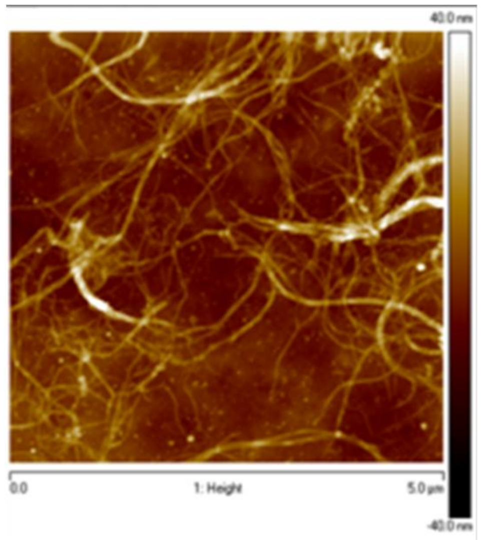




A) Eggs of *C. elegans*
B) Adult *C. elegans* eating cellulose nanofibrils

Summary – case 1

- Cytotoxicity
  - No indication of cytotoxic effects in HeLa229 cells were observed in HTD test
  - Some <u>indication of cytotoxicity</u> with the highest concentration (0.24 mg/ml)
- Sublethal effects
  - No sublethal toxicity in RNA inhibition test
- Genotoxicity
  - No indication of genotoxicity
- Nematode model
  - No systemic effects tested *in vivo* using Nematode



- ü FR3+FR4 tested can be considered non-toxic at concentrations lower than 0.12 mg/ml
- ü The material should not be judged toxic based solely on cytotoxicity data, but should be addressed in relation to other toxicity test results and the intended use of the product.

Case 2: Environmental safety

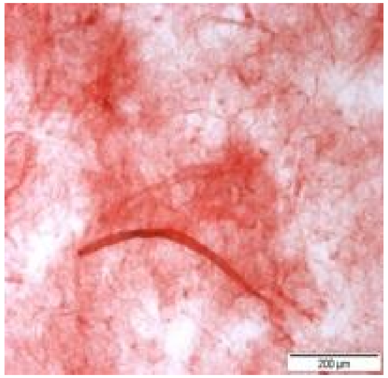
Vikman, M., Vartiainen, J., Tsitko, I., Korhonen, P. 2015. Biodegradability and Compostability of Nanofibrillar Cellulose-Based Products. J. Polymers Environ Vol. 23 (2015) No: 2, 206-215. doi: 10.1007/s10924-014-0694-3

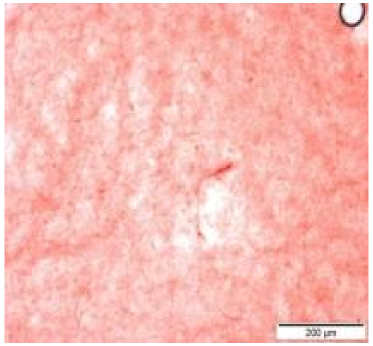
Kangas, H., Pitkänen, M., Vikman, M., Vartiainen, J., Tsitko, I. Cellulose nanofibrils (CNF) and CNF-based products. Biodegradability, Compostability and Safety. 2015 TAPPI International Conference on Nanotechnology for Renewable Materials, 22-25 June, Atlanta, USA.

Background & Approach

- The aim of the work was to obtain more information on the biodegradability and environmental safety of CNF and CNF-based products by
  - Studying the biodegradability of CNF gels
  - Studying the biodegradability and compostability of CNF films and papers containing CNF
  - Studying the ecotoxicity during biodegradation in the composting environment.

Studied materials

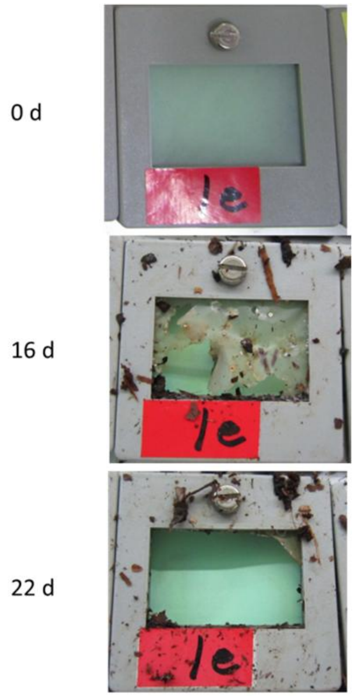




- Cellulose nanofibrils (CNF)
- CNF films
  - Vacuum filtration
  - Casting
- CNF Papers
  - CNF as an additive in the pulp furnish
  - CNF in the coating formulation

Methodology used

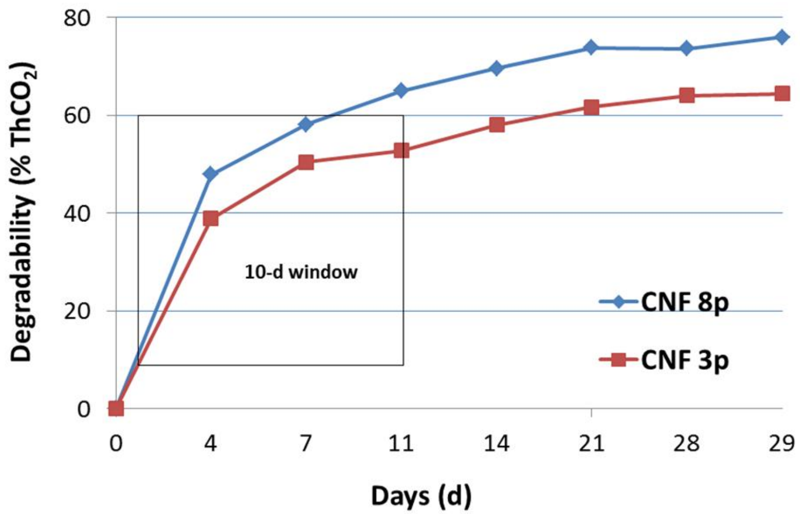
- Biodegradability of CNF gels - OECD 301B Ready Biodegradability – CO_2 evolution (Modified Sturm Test)
- Biodegradability of CNF films and papers (in the composting environment): EN 14046 Packaging. Method by analysis of released carbon dioxide.
- Compostability of CNF films and papers: EN 14045 Packaging. Based on the visual evaluation of the disintegration.
- Ecotoxicity during disintegration of CNF films and paper (in the composting environment): ISO 21338 standard method (Kinetic luminescent bacteria test).



CNF film1

Summary – case 2

- Fibrillation degree had an effect on biodegradability of CNF samples
  - the finer CNF material degraded to a larger extent during the test period.
- CNF films and papers were biodegradable according to criteria in the standard and also suitable for composting.
  - Papers containing CNF even degraded further than reference paper during the 65 d test period.
- No acute ecotoxicity was observed during biodegradation of CNF films and papers.



Safety testing of cellulose nanofibrils – some lessons learned from cases 2 & 3

- Selection of right toxicity testing methods crucial!
  - Not all suitable for gel-like materials, e.g. restriction of movement
  - ECHA's recommendations
    - E.g. bacterial testing not recommended for nanomaterials
- Contamination
  - False positives
- Addition of biocides
  - need to know the correct dose that does not affect the test result

Case 3: Risk assessment of polymer composites containing CNF

Background and motivation

- CNF offer sustainable alternative for manufacturing of light-weight composites with reduced carbon footprint
- However, little is known about the behavior of CNF at the different phases of the composites' life cycle
- Exposure to CNFs during production, use or end-of-life may lead to e.g.
  - inflammatory effects of employees
  - unwanted adverse effects in the environment

Ø Risk assessment performed to control and minimize any unwanted effects

Approach

Risk = **Exposure** × **Hazard**

Identified critical points

1. Occupational
2. Environment
3. Consumer use
4. End-of-life

Information from the literature

1. Human health
2. Environment

	Level of Exposure			
Concern Category	Low	Medium-low	Medium-high	High
Low	1	1	2	2
Medium-low	1	2	2	3
Medium-high	2	2	3	4
High	3	3	4	4

Hazard – information from the literature

Reported effects of CNF exposure

To humans

- Dose-dependent cytotoxicity
- Inflammatory effects
  - Potential resolution over time
  - Driven by material surface chemistry
- Biodurability in lungs
- Toxicity induced by chemical modification
- Raw material dependency – fibril dimensions

To environment

- Generally not acutely toxic to test organisms
- Surface charge had minimal influence
- Restriction of movement
- Raw material dependency – shape
- Biodegradability dependent on surface chemistry and fibrillation degree (available surface area)

Kangas, H., Pitkänen, M. (2016). Environmental, Health & Safety (EHS) aspects of cellulose nanomaterials (CN) and CN-based products. Nord. Pulp Paper Res. J. 31(2), 182-189.

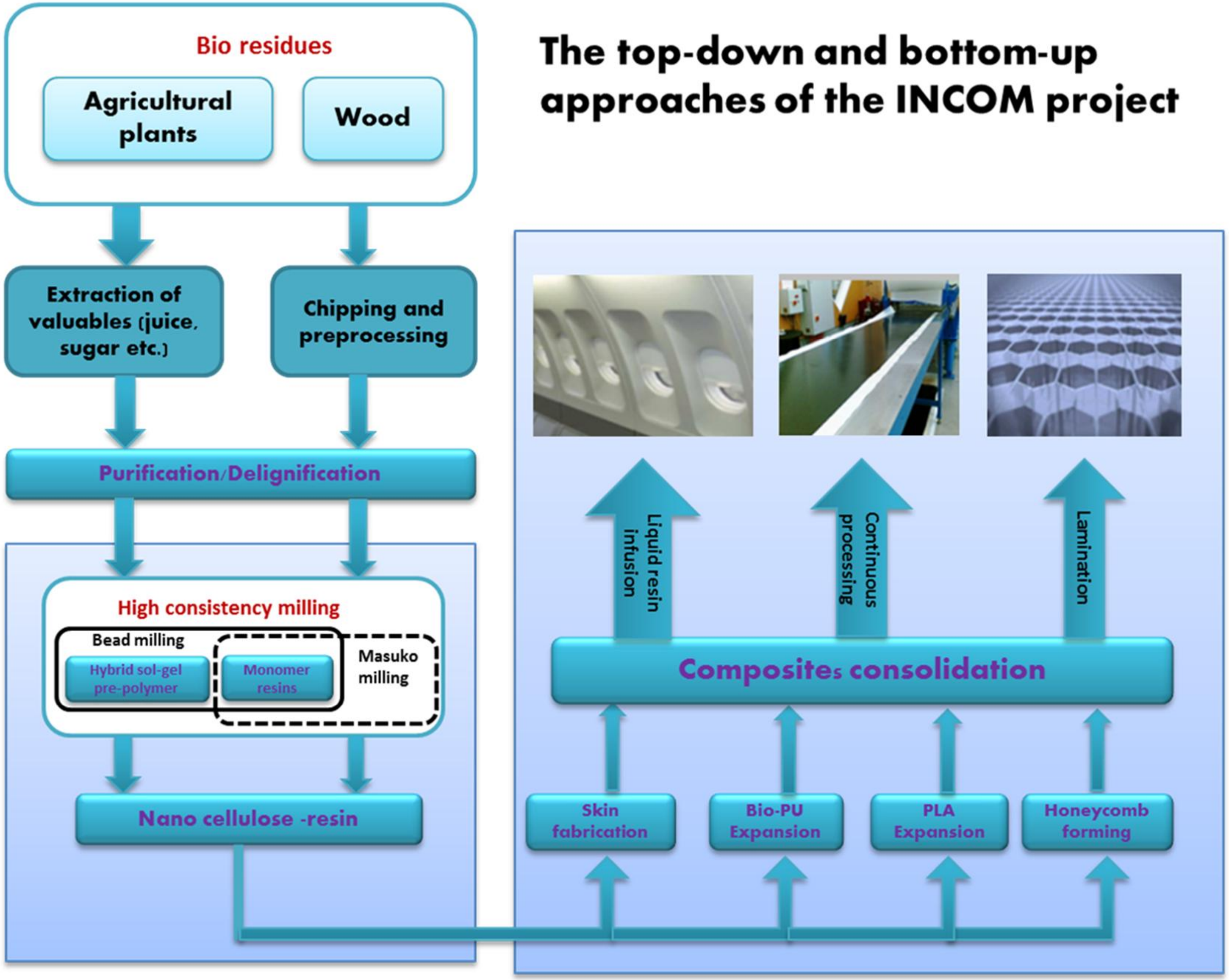
Critical points in nano-composite manufacturing

- The pre-production state, where the nanomaterials are at powder state, is the one with the highest risk.
  - carrying, handling and weighing
- Critical operations during production are mixing and pouring
- Exposure in the post-production stage during demolding, curing and cleaning of the equipment is also possible, but with lower probability.
- The final nanocomposite is unlikely to present a direct risk because nanoparticles are trapped into the solid resin.
- However, machining of the composite may lead to exposure – during manufacturing, cutting and milling of composites containing CNC, the the highest exposure was during cutting of the composite
- For carbon nanotubes (CNT), release was not observed from ductile composite materials, whereas from brittle materials release was observed.
- Weathering: all the studied materials exposed CNTs to the environment when the matrix was degraded by UV-light.

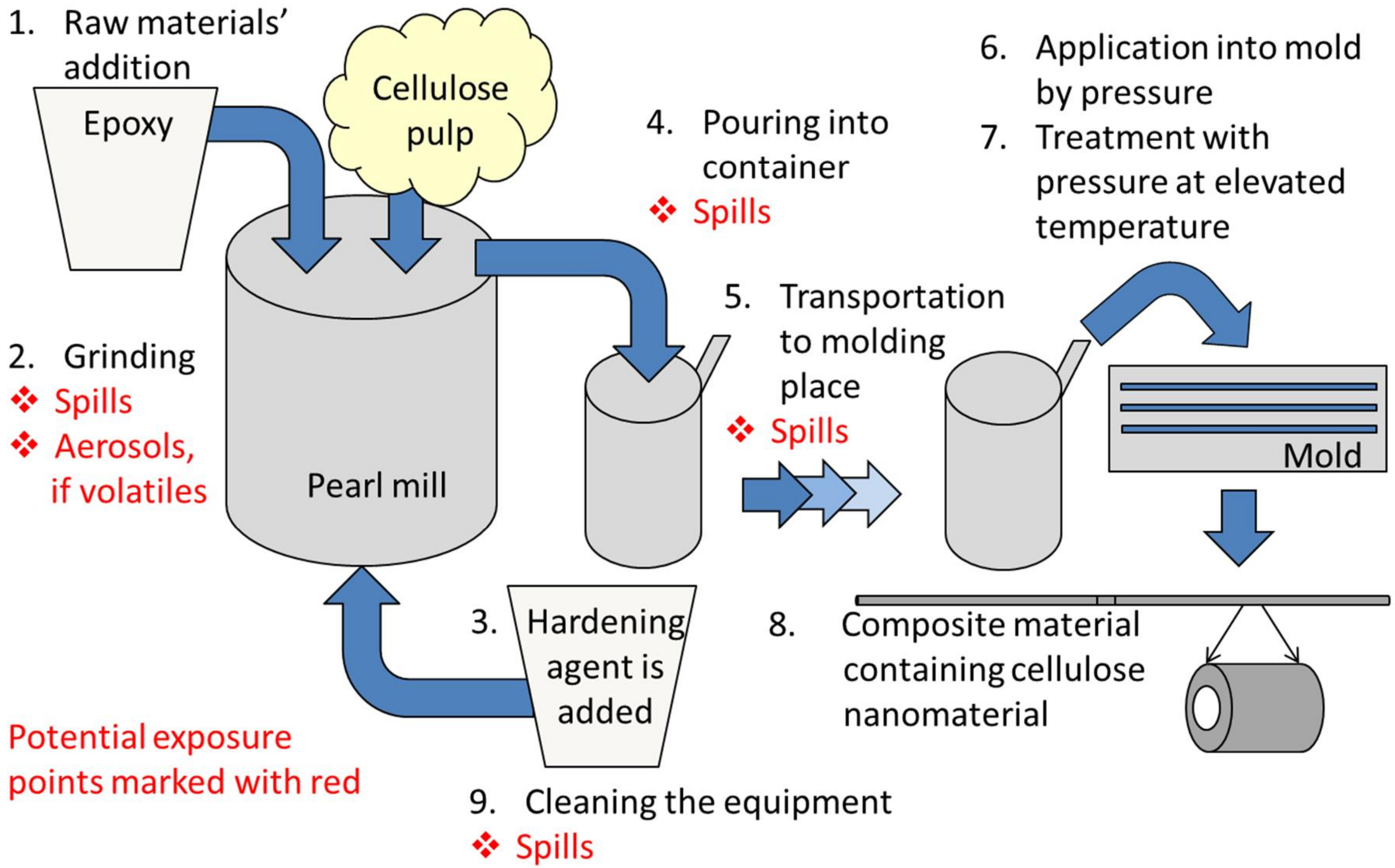
Soursa et al. Polymeric nanocomposites production risk assessment using different qualitative analyses. Occupational Safety and Hygiene II - Arezes et al. (eds). Taylor Francis Group, London 2014, pp. 25-30. ISBN-978-1-138-00144-2
Geraci C. L., Eastlake, A.C., Dunn, K.L. (2016) Progress in understanding worker exposure and risk for cellulose nanomaterials. Tappi International Conference on Nanotechnology for Renewable Materials. June 13-16, Grenoble.
Schlagenhauf et al. Release of Carbon Nanotubes from Polymer Nanocomposites. Fibers 2014, 2, 108-127; doi:10.3390/fib2020108

Exposure

Composite production in EU INCOM

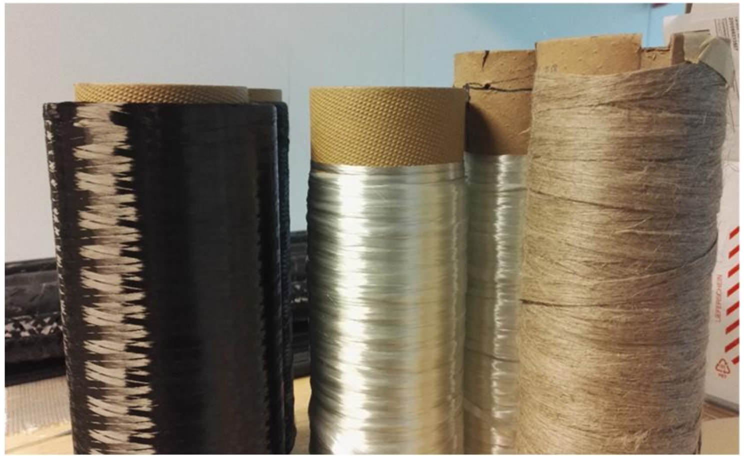


Lab scale production @VTT



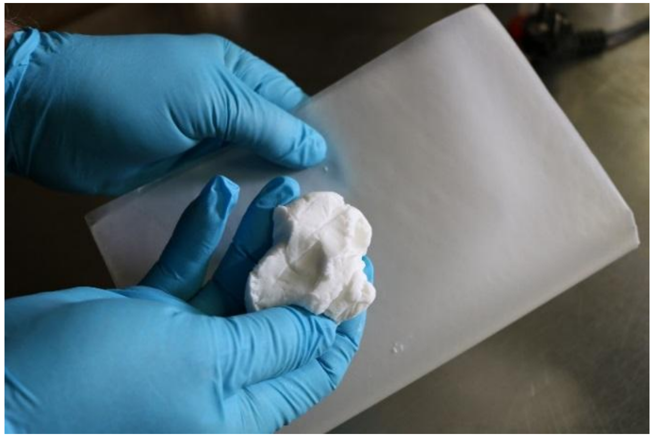
Industrial production @ small scale

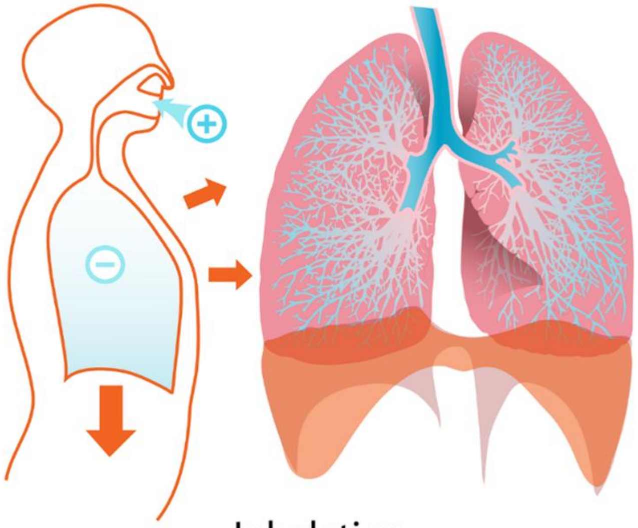
- **Resin transfer molding – RTM**
- Seed moulding compound – SCM
- Vacuum injection
- **Filament winding**



Main exposure routes

- Inhalation exposure
- Skin exposure





1. Potential occupational exposure – critical points

- Spills during mixing of CNF and polymer
- Pressure in the mould - RTM
  - Breakage or leakage of the piping
- Spills during winding
- Machining – cutting, sanding etc.
  - High probability for exposure according to previous studies
- Mitigation measures
  - Fume hood, fresh air hood

2. Potential environmental exposure during production

- Material waste
  - Raw materials
  - Finishing residues incl. dust
- Washing water
  - Containers
  - Floors, surfaces etc.
- Mitigation
  - Minimize raw material waste
  - Re-use of finishing residues
  - Minimize dust in the working space, fume hood
  - Suitable cleaning methods for spills

3. Consumer use

- Potential exposure depends on the end use and could take place e.g. by
  - Wear and tear
  - Machining, drilling, sanding etc.
- Case example: sport equipment
  - Cutting into size – not probable
  - Polishing – not needed
  - Accidental snapping

4. End of life

- Depends on the end use
  - Recycling
  - Re-use
  - Waste disposal: inceniration, landfill
- In case of sport equipment, inceniration is the most probable route
  - CNFs burned forming carbon

Conclusions – risk assessment

- No major concern found in lab scale or industrial production @ small scale
- As typical for risk assessment, exposure during the production steps and hazard related to the materials should be evaluated case-by-case
    - Increasing knowledge of hazardous properties and behavior of nanomaterials calls for continual review of the risk assessment and management measures

Acknowledgements – case 3

- The research leading to these results has received funding from the European Union Seventh Framework Programme under grant agreement no 608746.
- Co-authors Marja Pitkänen and Lisa Wikström

Risk assessment according to European Commission Recommendation

Risk assessment based on

- European Commission's *Guideline on the protection of the health and safety of workers from the potential risks related to nanomaterials at work*

European Commission. Guidance on the protection of the health and safety of workers from the potential risks related to nanomaterials at work. 2014. 63 p.

A 7-step procedure

1. Identification
   - Do nanomaterials exist in the workplace?
   - Check the inventories of substances applied and supplied
   - Material safety data sheets (MSDS) as primary sources of information
   - Contact the supplier / manufacturer if in doupt
   - REACH, CLP, European Observatory for Nanomaterials https://euon.echa.europa.eu
2. Hazard assessment
   - Information about hazardous properties needed: labels, SDS, occupational exposure limit values and scientific publications.

A 7-step procedure

3. Exposure
   - Consider all the routine operations and other foreseeable events in detail
   - Some clarifying questions
     - Is the material dusty or the process likely to generate dusts or aerosols?
     - Does the process include cutting, shearing, grinding, abrasion, or other mechanical release?
     - How often is exposure likely to occur?
   - Four classes of potential exposure
4. Risk categorisation

	Level of Exposure			
Concern Category	Low	Medium-low	Medium-high	High
Low	1	1	2	2
Medium-low	1	2	2	3
Medium-high	2	2	3	4
High	3	3	4	4

A 7-step procedure

5. Detailed risk assessment
   - Needed for risk levels 3 & 4
   - Quantative assessment of exposure
6. Risk management
   1) elimination or substitution
   2) process modification
   3) isolation or enclosing
   4) engineering control
   5) administrative control
   6) personal protective equipment (PPE)
7. Review
   - Regular check-up

Recommendations & next steps

- The safety of cellulose nanomaterials and CNM-based products should be evaluated case by case
- Co-operation for the development of testing methods needed
  - Validation / standardisation
- Increased understanding of the knowledge gaps
  - Short-term / long-term
- Pro-active communication between academia, producers, authorities etc.
  - Data from actual production needed for risk analysis